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<b>(54) Title:</b> GLASS ARTICLE  <b>(57) Abstract</b> <p>A glass coating composition including an effective amount of at least one inorganic or organic polymeric component; and at least one reinforcing component incorporated therein; the glass coating composition being such that when coated on a glass substrate it strengthens and toughens the article.</p>		

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GLASS ARTICLE

The present invention relates to glass articles including toughened glass articles and to a method of preparing such glass articles.

5       Silica based glasses, including the widely-used soda-lime container glass, are isotropic elastic solids. They are chemically homogeneous, with all the constituent atoms strongly bonded to one another, but with no long-range or periodic order.

10       Estimates based on the nature of the interatomic forces indicate that strains of up to 20% should occur before rupture occurs: this is equivalent to strengths in the range 10-20 GPa. For normal samples, observed strengths usually are less than one hundredth of this theoretical level;  
15       moreover, samples which have received nominally identical treatment show a wide variation in their individual strengths.

It is well established that fracture of glass occurs at pre-existing flaws or microcracks, and this limits the attainable strength. Most glass articles possess surface  
20       microcracks which have been produced by abrasion, indentation or impact of the surface by another hard body, or by another glass article. The mechanism of microcrack initiation in pristine surfaces has yet to be established, however. Even when mechanical damage to a glass surface has been avoided,  
25       the strength may not be any larger: in this case, the flaws responsible may be foreign particles which have become fused to the surface and which generate microcracks around themselves as a result of differential thermal expansion when the body is cooled. Such surface inclusions may be airborne

- 2 -

dust particles present during the heat treatment of the glass, and temperatures well below the softening point of the glass will suffice to develop strongly-bonded inclusions, which then act as significant strength-limiting flaws. Also, atmospheric moisture acts detrimentally on a glass surface, producing corrosion products; these are a form of foreign inclusion, and have the same strength-limiting effect.

Some attempts in the prior art to increase the strength of glass have been partially successful. These procedures are based on the fact that if the glass surface is placed under compression, extra work must be done to overcome this compression before any pre-existing microcrack can be widened and thereby produce catastrophic failure. One such prior art procedure compresses the surface of a glass body by chilling with an air blast at a time when the glass was plastic. Then, under normal cooling, the thermal shrinkage of the bulk compresses the hardened surface layer. This procedure has been much used for toughened glass plates.

In another procedure, the sodium in the surface layer of glass is exchanged for potassium in a molten salt bath. Since the potassium ions occupy a greater volume than the sodium ions they have replaced, the surface layer is placed under a compressive stress. This procedure is costly, however, and cannot be applied reasonably to glass containers that are made in large numbers.

Accordingly, it is an object of the present invention to overcome, or at least alleviate, one or more of the difficulties related to the prior art.

Accordingly, in a first aspect there is provided a glass coating composition including an effective amount of

at least one inorganic or organic polymeric component; and

5       ~~at least one reinforcing component incorporated~~  
therein.

The glass coating composition according to the present invention, when coated on a glass article, strengthens and toughens the article. The coating  
10       advantageously adheres strongly to the glass substrate and possesses a high tensile strength of itself.

Whilst we do not wish to be restricted by theory, it is postulated that the coating formed from the glass coating composition lies across any pre-existing, strength-limiting  
15       flaws in the glass surface. Under the action of any applied tensile load, the stress across any flaw would then be carried by the coating. Thus, extra work would have to be done before the load carrying effect of the coating broke down, which would then allow the microcracks in the glass to  
20       widen and cause failure of the glass.

Additionally, the coating formed from the glass coating composition may protect the glass surface from abrasion, indentation, or any other such damage leading to the production of strength limiting flaws.

25       The at least one inorganic or organic polymeric component of the glass coating composition may be of any suitable type which will provide the required high tensile strength. A water soluble or water insoluble polymer may be used. Where a water solubl polymer is used the coating

- 4 -

composition may be rendered water resistant as discussed below. A natural or synthetic organic polymer may be used as the polymeric component. A synthetic organic polymer may be selected from acrylic polymers including acrylate and methacrylate polymers or copolymers, acrylamide or methacrylamide polymers or copolymers thereof, urethane polymers or copolymers thereof, alkyd resins, or mixtures thereof.

Preferred acrylic polymers include polyacrylamide and polymethylmethacrylate.

Alkyd resins ("Glyptal" resins), may be used alone, or with the inclusion of one or more copolymers to modify their properties in a manner known per se. These resins may be provided in a form that is soluble in common organic solvents such as alcohol, applied to the glass, dried, then converted to the final crosslinked or cured form thermally at temperatures near 200°C ("stoving varnishes"), or crosslinked with reagents such as melamine to further modify the properties according to known art. Alkyd resins are obtainable commercially in an extremely wide range of formulations, and admixtures with copolymers and crosslinking agents.

The preferred polyurethanes may be selected from the large range of formulations available commercially.

Polyurethane is known to have excellent adhesion to glass, and has been proposed as a useful coating (e.g. Vaporcure process). There is a wide range of polyurethane products available and a correspondingly wide range of properties. For the present application, a commercial

two-part coating material was purchased (Epiglass reaction lacquer). Preliminary trials showed that this coating formed hard adherent films on freshly fired slides.

Polyurethanes are produced from a reaction between a polyhydroxyl compound (polyol) and a polyfunctional isocyanate. Typical reactants could be propylene glycol and toluene diisocyanate with a catalyst of tin octoate. The commercial two-part PU coatings contain partly polymerised polyol/diisocyanate: one part has unreacted hydroxyl groups and catalyst, the other part has an excess of isocyanate. When the two components are mixed they react to form a gelatinous solid in about an hour; reaction then continues to form a rigid polymer. Complete reaction at room temperature takes about 3 days.

The period of 3 days required to achieve complete reaction was inconvenient, so further investigations have been conducted at various temperatures and times to investigate thermal acceleration of the polymerization. It was found that heating to 80°C for 2 hours was sufficient to give a tough adherent film.

A protein polymer for example a casein polymer may be used as a natural polymeric component.

Alternatively, or in addition, a low melting silicon polymer may be used. A low melting glass may be used.

The at least one polymeric component may be present in any suitable effective amounts. The polymeric component may comprise from approximately 40 to 95% by weight, based on the total weight of the glass coating composition. A polymeric component content of about 50 to 95% by weight is

- 6 -

preferred.

The at least one reinforcing component of the glass coating composition may have a platelet-type structure. The reinforcing component having platelet-type structure may be a  
5 silicon carbide or vermiculite product, for example an exfoliated vermiculite.

The reinforcing component may alternatively or in addition include a component having a fibrous structure, organic, inorganic or mineral fibres, preferably high-modulus  
10 whiskers or fibres. The reinforcing component having a fibrous structure may include silicon carbides, silicon nitrides, alumina, metals or mixtures thereof.

However, it is preferred that silicon carbide (SiC) including silicon carbide whiskers are not used in  
15 conjunction with polyacrylate polymers, alkyd resins.

A vermiculite product has the advantage that the particles are platelets typically approximately 5  $\mu$ m diameter and about 3nm thick, which do not represent any biological hazard, as may be encountered with product having a fibrous  
20 structure. Preferably, flakes would all lie parallel in a coating and be bonded to each other, and to the glass surface by the polymeric component. Where whiskers or fibres are present, these may be in any suitable configuration including felts, oriented weaves and lay-ups so as to provide desired  
25 mechanical properties to the coating.

The reinforcing component may be present in the glass coating composition in any suitable effective amount. The reinforcing component may be present in amounts of from approximately 5 to 60% by weight, based on the total weight



of the glass coating composition. A reinforcing component of approximately 5 to 40% by weight based on the total weight of the glass coating composition is preferred.

In a preferred aspect of the present invention the glass coating composition may further include an effective amount of at least one coupling agent.

The at least one coupling agent may function to improve adhesion of the polymeric component to the reinforcing component and/or to the glass substrate when, in use, the coating composition is coated onto such a substrate. The coupling agent may also function to improve the water resistance of the coating on curing.

The at least one coupling agent may be a silane product. An amino silane product may be used. (N,N-diethyl-3-aminopropyl)trimethoxysilane is preferred.

The at least one coupling agent may be present in the glass coating composition in any suitable effective amount. The at least one silane coupling agent may be present in an amount of from approximately 0.1 to 1% by weight based on the total weight of the glass coating composition.

In a further preferred aspect of the present invention, where a water soluble polymeric component is used, the glass coating composition may further include an effective amount of at least one cross-linking agent. The cross-linking agent may be a heat-, or radiation-curable cross-linking agent. A cross-linking agent such as a glyoxal formaldehyde may be used. The at least one cross-linking agent may be present in the glass coating composition in any

suitable effective amount. The cross-linking agent may be present in amount of from 0 to approximately 50%, preferably approximately 5 to 50%, more preferably approximately 7.5% to 10% by weight based on the total weight of the glass coating composition.

The glass coating composition according to the present invention may further include other compounding ingredients. Compounding ingredients such as colourants, fillers, solvents, dispersants, surfactants, extenders, and the like may be included.

The glass coating composition may be provided in the form of a solution or dispersion in a suitable solvent. An aqueous solvent or organic solvent or mixtures thereof may be used. An alcohol solvent, e.g. methanol or ethanol may be used. An aqueous solution is preferred.

In a preferred form the glass coating composition includes approximately 40 to 70% by weight of polyacrylamide; approximately 30 to 60% by weight of vermiculite; and approximately 0.1% to approximately 0.5% by weight of (N,N-diethyl-3-aminopropyl)trimethoxysilane.

In a further preferred form the glass coating composition may include

approximately 80 to 95% by weight of a polyurethane polymer; and

approximately 5 to 15% by weight silicon carbide.

In a further aspect of the present invention there is provided a toughened article including

a glass article, and

a glass coating on at least one surface thereof,

formed from a glass coating composition including

an effective amount of at least one inorganic or organic polymeric component; and

at least one reinforcing agent incorporated therein;

5 the glass coating being such that when coated on the glass article, it strengthens and toughens the article.

The glass article may be formed from a silica based glass. The glass article may be formed from a soda-lime type glass. The glass article may be a shaped article. The glass  
10 article may be a container such as a bottle, jar or like vessel.

The glass article may be subjected to a surface purification step prior to application of the coating. The glass article may be prepared for coating by way of a  
15 cleaning or other step as discussed below.

The glass coating composition may include approximately 40 to 70% by weight of polyacrylamide; approximately 30 to 60% of vermiculite; and approximately 0.1% to approximately 0.5% by weight  
20 of a coupling agent, preferably (N,N-diethyl-3-aminopropyl)-trimethoxysilane.

Alternatively, the glass coating composition may include

approximately 80 to 95% by weight of a polyurethane  
25 polymer; and

approximately 5 to 15% silicon carbide.

In a still further aspect of the present invention there is provided a process for preparing a toughened article including

- 10 -

providing a glass article; and  
a glass coating composition including  
an effective amount of at least one inorganic or  
organic polymeric component; and

5 at least one reinforcing component incorporated  
therein;

the glass coating composition being such that when  
coated on a glass substrate it strengthens and  
toughens the article;

10 contacting the surface of the glass article with the  
glass coating composition; and

drying the coated glass article so formed.

The glass article may be a glass container,  
preferably a soda-lime type glass container as discussed  
15 above.

The glass coating composition may be provided in the  
form of an aqueous solution.

In a preferred form the glass coating composition  
may further include at least one coupling agent. Where a  
20 coupling agent is present, the process for preparing a  
toughened article may include the preliminary step of

mixing the coupling agent with the polymeric  
component and at least one reinforcing component for  
a time sufficient to allow the coupling agent to  
25 hydrolyse and/or to interact with the reinforcing  
component prior to contact with the surface of the  
glass article.

In a further preferred form, the at least one  
reinforcing agent of the glass coating composition includes

exfoliated vermiculite. Where an exfoliated vermiculite is present, the process for preparing a toughened article may further include the preliminary step of

subjecting the vermiculite to a conversion process to produce an exfoliated vermiculite.

For example, the vermiculite may first be reacted with sodium chloride to form a sodium vermiculite. The sodium vermiculite may then be reacted with an N-butylamine hydrochloride to form the final exfoliated product.

In a still further preferred form, the process for preparing the toughened article may include the preliminary step of

subjecting the glass article to a surface preparation step.

The surface preparation step may include a physical or chemical cleaning step. Various solvents, acidic or basic polishers or etchers may be used. Alternatively or in addition an electrical discharge treatment may be included.

However, the most effective surface preparation step includes a heat treatment step. Preferably, the glass article is subjected to a firing in air at elevated temperature for a time sufficient to clean the surface. The heated glass may be then subjected to slow cooling, for example at room temperature.

The heat treatment step may be conducted at temperatures of approximately 350 to 450°C and above. Preferably a temperature of 400°C is preferred. Lower firing temperatures were found to be ineffective. Similarly, temperatures significantly higher than 450°C are to be

- 12 -

avoided as there is a risk of compositional changes in the surface.

These surface preparations may be combined with various storage procedures to minimise atmospheric corrosion prior to coating of the freshly cleaned surfaces. For example, the glass articles may be stored under dry nitrogen after cleaning.

As stated above, the glass coating composition may preferably be provided in the form of an aqueous solution. The aqueous solution of the glass coating composition may be coated onto the surface of the glass article in any suitable manner. The glass coating composition may be coated onto the surface as a film for example using kiss coating, doctor rolls, gravure rolls, immersion coating techniques or similar techniques. The glass coating composition may be sprayed onto the glass surface in any known manner.

Once the glass coating composition is coated onto the surface, the film so formed may then be dried to remove excess solvent. Drying times and temperatures will vary depending, for example, on the composition of the composition and thickness of coating. The drying step may be conducted in air at room temperature for a period of approximately 12 to 48 hours, preferably for approximately 24 hours.

In a preferred aspect of the present invention, the process of preparing the toughened article may further include the further step of curing the coated glass article. The curing step may take any suitable form depending on the cross-linking agent present. Where the natural or synthetic organic polymer is a curable polymer, the curing step may

include heating the coated glass article at elevated temperature for a period sufficient to provide substantially complete cure. Temperatures of the order of 75 to 100°C, preferably approximately 80 to 90°C may be used.

5       The present invention will now be more fully described with reference to the accompanying examples. It should be understood, however, that the description following is illustrative only and should not be taken in any way as a restriction on the generality of the foregoing description.

10                   EXAMPLE 1

(a) Test Rig

15       Glass microscope slides obtained commercially were used for testing. Strength testing of these, or of coated glass slides by standard 4-point bend procedures would be futile since the slides have cut edges and thus extensive arrays of strength-limiting flaws around these edges produced by the cutting process. These would control the apparent strength of any slide, and the results would be atypical of the glass itself. Flame polishing of the edges could reduce this effect, but this procedure would lead to evaporative loss of sodium from the glass, and the consequent compositional change would again lead to spurious results.

20       The strength testing rig used consisted of two rings of different diameters that pressed on each side of the glass surface. The rings were constrained to be coaxial by a suitable jig, which was placed in a standard testing machine (Instron). This test rig was thus a biaxial 4-point bend machine.

Fracture of the test slides was confined to the

- 14 -

region inside the larger ring, so that the effects of the edges were eliminated or minimised. In each case, the test slide was coated on the compressive side with transparent adhesive tape so that the pieces could be retained and the origin of fracture confirmed to be within the test ring.

Test slides were indented with a Vickers diamond indenter at 1 Kg load so as to make a single flaw that would control the strength of the slide. In all test cases, it was confirmed that the fracture originated at this flaw. The purpose of this procedure was to ensure a reasonably constant base value for the strength of untreated glass, so that the effect of any coating would be immediately apparent. Also, any increase in strength above the base value resulting from any applied coating would represent a toughening effect due to that coating.

(b) Preparation of exfoliated vermiculite

In accordance with a known procedure, natural vermiculite is converted to the sodium form by refluxing 400g in 1000 ml water containing 390g sodium chloride for 24 hours. The product is washed with water to remove chloride.

The sodium vermiculite is converted to the n-butylamine form by reaction with n-butylamine hydrochloride. The sodium vermiculite is refluxed for 24 hours in a solution consisting of 1000 ml water, 400ml n-butylamine and sufficient (about 400ml) concentrated hydrochloric acid to make the pH 5.2

The n-butylamine product is repeatedly washed until it swells to several times its original volume. It is then milled in a high-speed blender or stirrer producing high



shear. The final product is a nacreous sol of platelets approximately 5  $\mu$ m diameter and 2nm thick. This is concentrated by centrifugation to about 20% solids by weight.

(c) Cleaning of test glass slides

5 The most effective procedure was found to be a firing in air to 400°C for one hour followed by a slow cooling to room temperature immediately before coating. Lower firing temperatures were ineffective, whilst at higher temperatures there was the risk of compositional changes in the surface because of component volatility (resulting in  
10 spurious mechanical properties) or healing of the artificial indentation flaw.

In a preferred form of the invention, a coating consisting of 60% by weight of polyacrylamide (PAA), and 40%  
15 by weight of a reinforcing filler of exfoliated vermiculite flakes is applied to freshly cleaned container glass.

Thus 14.3g of an aqueous solution containing 20.75% by weight of P-26 PAA (Cyanamid Corp.) is mixed with 10.7g of 18.47% vermiculite sol and 50g of water. After thorough  
20 mixing, 0.05g of (N,N-diethyl-3-aminopropyl)trimethoxysilane (DEAPTMS) is added as a coupling agent. The DEAPTMS is allowed to hydrolyse and interact with the vermiculite for 24 hours before the mixture is applied to the glass.

The mixture is applied to freshly cleaned glass as a  
25 film approximately 0.1mm thick by means of a Doctor Blade apparatus. The film is allowed to dry in air at room temperature for 24 hours, then cured at 85°C to render the coating water resistant.

The modulus of rupture (MOR) measured for indented

- 16 -

uncoated glass slides was  $56 \pm 2$  MPa: the MOR measured for indented slides coated as above was  $87 \pm 4$  MPa, a significant enhancement.

MOR measurements for slides coated with PAA/vermiculite compositions varying from 0 to 100% PAA showed that there was a broad maximum in the strength enhancement, and that the composition with 60% PAA was close to optimum.

#### EXAMPLE 2

Pu/SiC composites were prepared by adding SiC whiskers to freshly mixed PU resin. It was intended to apply composites of 3 different whisker amounts as well as unfilled PU to standard cleaned slides and acid washed slides. SiC whiskers were dispersed ultrasonically in the resin, since simple mixing was ineffective.

The quantity of SiC whiskers that could be added to the PU resin was limited to a narrow range by the viscosity requirements of the film spreader. The unreinforced PU coating was applied by brush.

The complete coating procedure used was as follows:

- (a) A set of slides were fired at  $400^{\circ}\text{C}$  and cooled.
- (b) The slides were Vickers indented at 1 Kg.
- (c) The slides were refired at  $200^{\circ}\text{C}$  and cooled.
- (d) Immediately after the last firing the slides were mounted for coating.
- (e) A small quantity of the PU resin was mixed and the whiskers were added.
- (f) The slides were coated on the film spreader.
- (g) After 2 hours at room temperature the samples were

heated to 80°C for 2 hours.

(h) The coated samples were tested in the normal way on the biaxial rig.

A glass coating consisting of 94% to 91% by weight of polyurethane, and 6% to 9% by weight of reinforcing filler of silicon carbide whiskers is applied to freshly cleaned container glass.

Thus 8.8g of silicon carbide whiskers (Tateho Corp., Japan: 0.5  $\mu$ m diameter, aspect ratio 10) were added to 91.2g of freshly-mixed two-part liquid polyurethane material (Epiglass Reaction Lacquer) and dispersed uniformly in an ultrasonic bath. Test glass was cleaned by firing at 400°C, provided with a strength-limiting flaw by indenting at 1Kg, refiring at 200°C, and coated with the mixture to a thickness of approximately 0.1mm. The test glass specimens were kept at room temperature for 2 hours to allow the coating mixture to set, then heated at 80°C for 2 hours to effect a full thermal curing of the polyurethane.

Additionally, test glass was prepared and coated as above, but using no whiskers in the polyurethane.

Also, test glass was prepared as above, but provided with no coating.

The MOR measured for indented uncoated glass was 56 $\pm$ 2 MPa: the MOR measured for glass coated with polyurethane alone was 70 $\pm$ 4 MPa: the MOR measured for glass coated with polyurethane containing 8.8% by weight silicon carbide whiskers was 115 $\pm$ 19 MPa, a significant enhancement.

The area under the stress vs., displacement curves produced for each specimen in the fracture testing rig is a

- 18 -

measure of the work of fracture, or toughness of the test specimen. Typical stress vs. displacement curves for uncoated indented glass, indented glass coated with polyurethane only and indented glass coated with polyurethane  
5 containing 8.8% by weight silicon carbide whiskers are shown in Figures 1, 2 and 3. The relative areas under the curves are in the ratio 1.0 : 2.1 : 40.0 respectively, so that compared to uncoated glass, the coating of polyurethane alone toughens the glass by a factor of 2.1, while the silicon  
10 carbide whisker/polyurethane coating toughens the glass by a factor of 40, a substantial increase.

Further, the decay of the stress/displacement curve to zero at a displacement near 1.2mm, for glass coated with silicon carbide whiskers/polyurethane, of which Figure 3 is a  
15 typical example, does not represent failure of the test piece, as does the corresponding parts of the curves in Figures 1 and 2. Here instead, the stress applied by the testing machine was removed because the test piece had deformed (without failure) to such an extent that the testing  
20 rig no longer performed its function properly, a further demonstration of the resistance to failure supplied by this coating. On relief of the stress, the test piece returned to its original form. For calculation of the MOR, the largest value of the applied stress observed was used, since no  
25 stress at rupture per se could be determined.

All specimens were examined microscopically after testing. Uncoated glass and glass coated with polyurethane alone had fractured cleanly and in the manner typical of a brittle material. There was some crack branching in the

coating layer, an energy absorption process that accounted for the small increase in toughness of glass so coated. Microscopical examination of the glass coated with silicon carbide whiskers/polyurethane after fracture testing showed  
5 that the glass itself had a high density of fine cracks originating from the indentation: the production of these would have required far more work than that required to produce a single crack. The integrity of the piece was maintained by the coating. Also, cracks in the coating were  
10 heavily branched, indicative of strong energy absorption or stress dissipation processes occasioned by the presence of the whiskers, while there was evidence that additionally, resistance to the widening of cracks in the coating under stress was provided by the whiskers bridging across such  
15 cracks, so that energy was absorbed by whisker pull-out, a well-known toughening process.

Similar measurements made on glass similarly prepared and coated with polyurethane containing 6.2% by weight of silicon carbide whiskers gave results that did not  
20 differ significantly from those described above for polyurethane containing 8.8% by weight of silicon carbide whiskers.

The test results for the PU/SiC composites are shown in Tables 1 to 7 and illustrated in Figures 4 to 10,  
25 respectively.

- 20 -

TABLE 1

As Fired Slides, Uncoated

Indented/Refired these slides were fired at 400°C  
then indented then reheated to 200°C.

5 No coating was applied.

	SAMPLE				SAMPLES	
	NUMBER	DEPTH	LOAD	MOR (MPA)	21	
19	1	0.94	98	54	WEIBULL	
	2	0.94	103	57	MEAN: 30.28	
	3	0.92	104	60		
	4	0.92	97	56	FIT OF	
	5	0.92	95	55	MEAN: 0.8625	
	6	0.92	96	56		
	7	0.92	102	59		
15	8	0.96	99	53	WEIBULL	
	9	0.96	103	55	MEDIAN: 32.33	
	10	0.96	103	55		
	11	0.96	103	55	FIT OF	
	12	0.94	95	53	MEDIAN: 0.8548	
20	13	0.94	103	57		
	14	0.94	100	56		
	15	0.94	100	56	MEAN	
	16	0.96	104	55	M.O.R.: 55.58	
	17	0.96	101	54		
25	18	0.96	105	56	STD.	
	19	0.96	103	55	DEV.: 1.84	
	20	0.96	100	53		
	21	0.96	107	57		

TABLE 2

Fired Slides PU

Indented Slides. These slides were fired at 400°C  
and then coated with PU. No SiC whiskers were added.

5	SAMPLE				SAMPLES	
	NUMBER	DEPTH	LOAD	MOR (MPA)	22	
	1	0.93	135	77	WEIBULL	
	2	0.93	126	72	MEAN:	20.06
	3	0.93	127	72		
10	4	0.93	124	70	FIT OF	
	5	0.92	124	72	MEAN:	0.9658
	6	0.92	132	77		
	7	0.93	128	73		
	8	0.93	133	76	WEIBULL	
15	9	0.93	117	66	MEDIAN:	21.40
	10	0.93	127	72		
	11	0.9	104	63	FIT OF	
	12	0.9	108	65	MEDIAN:	0.9596
	13	0.91	112	66		
20	14	0.91	114	68		
	15	0.92	116	67	MEAN	
	16	0.92	120	70	M.O.R.:	70.22
	17	0.91	120	71		
	18	0.91	108	64	STD.	
25	19	0.93	128	73	DEV.:	3.68
	20	0.93	125	71		
	21	0.93	121	69		
	22	0.93	127	72		

- 22 -

TABLE 3

Fired slides &amp; 6.2% SiC/PU

Indented slides &amp; (US disp.)

These slides were fired at 400°C and then

5 coated with 6.2% SiC/PU. The coating was  
dispersed with ultra sound.

	SAMPLE				SAMPLES	
	NUMBER	DEPTH	LOAD	MOR (MPA)	22	
	1	0.92	240	139	WEIBULL	
10	2	0.92	227	132	MEAN: 4.85	
	3	0.91	144	85		
	4	0.91	257	152	FIT OF	
	5	0.88	128	81	MEAN: 0.8927	
	6	0.88	222	141		
15	7	0.92	226	131		
	8	0.92	150	87	WEIBULL	
	9	0.92	230	133	MEDIAN: 5.14	
	10	0.92	162	94		
	11	0.91	243	144	FIT OF	
20	12	0.91	144	85	MEDIAN; 0.8758	
	13	0.87	203	132		
	14	0.87	141	91		
	15	0.88	237	150	MEAN	
	16	0.88	135	86	M.O.R.: 113.47	
25	17	0.92	174	101		
	18	0.92	187	108	STD,	
	19	0.89	170	105	DEV.: 23.68	
	20	0.89	153	95		
	21	0.92	208	121		
30	22	0.92	175	102		



TABLE 4

Fired Slides & 7.6% SiC/PU

Indented Slides. These slides were fired at 400°C

and then coated with 7.6% SiC/PU. The coating was not

5 dispersed with ultra sound.

SAMPLE					SAMPLES
NUMBER	DEPTH	LOAD	MOR (MPA)		22
	1	0.92	135	78	WEIBULL
	2	0.92	137	79	MEAN: 7.57
10	3	0.93	160	91	
	4	0.93	194	110	FIT OF
	5	0.92	157	91	MEAN: 0.8326
	6	0.92	133	77	
	7	0.96	157	84	
15	8	0.96	165	88	WEIBULL
	9	0.93	145	82	MEDIAN: 8.05
	10	0.93	150	85	
	11	0.93	195	111	FIT OF
	12	0.93	126	72	MEDIAN: 0.8204
20	13	0.92	130	75	
	14	0.92	140	81	
	15	0.95	152	83	MEAN
	16	0.95	170	92	M.O.R.: 88.33
	17	0.92	157	91	
25	18	0.92	192	111	STD.
	19	0.96	143	76	DEV.: 11.95
	20	0.96	155	83	
	21	0.93	161	91	
	22	0.93	195	111	

- 24 -

TABLE 5

Fired Slides &amp; 8.8% SiC/PU

Indented slides (US disp.)

These slides were fired at 400°C and then  
 5 coated with 8.8% SiC/PU. The coating was  
 dispersed with ultra sound.

	SAMPLE				SAMPLES	
	NUMBER	DEPTH	LOAD	MOR (MPA)		22
10	1	0.88	171	108	WEIBULL	
	2	0.88	200	127	MEAN:	6.31
	3	0.87	257	167		
	4	0.87	195	126	FIT OF	
	5	0.92	164	95	MEAN:	0.8461
15	6	0.92	264	153		
	7	0.92	190	110		
	8	0.92	250	145	WEIBULL	
	9	0.93	176	100	MEDIAN:	6.71
	10	0.93	163	93		
20	11	0.9	180	109	FIT OF	
	12	0.9	200	121	MEDIAN:	0.8348
	13	0.93	190	108		
	14	0.93	205	116		
	15	0.87	180	117	MEAN	
25	16	0.87	177	115	M.O.R.:	114.75
	17	0.9	175	106		
	18	0.9	193	117	STD.	
	19	0.93	160	91	DEV.:	19.17
	20	0.93	161	91		
30	21	0.91	172	102		
	22	0.91	180	107		

TABLE 6

Acid Washed Slides Indented

These slides were fired at 400°C then washed in

1M HNO<sub>3</sub>. No further treatment was performed.

5	SAMPLE		SAMPLES		
	NUMBER	DEPTH	LOAD	MOR (MPA)	22
10	1	0.9	110	67	WIEBULL
	2	0.9	113	68	MEAN: 16.83
	3	0.91	115	68	
	4	0.91	113	67	FIT OF
	5	0.93	115	65	MEAN: 0.9764
	6	0.93	113	64	
	7	0.91	113	67	
	8	0.91	107	63	WEIBULL
15	9	0.93	105	60	MEDIAN: 17.94
	10	0.93	105	60	
	11	0.93	100	57	FIT OF
	12	0.93	113	64	MEDIAN: 0.9691
	13	0.93	102	58	
20	14	0.93	107	61	
	15	0.9	103	62	MEAN
	16	0.9	111	67	M.O.R.: 62.96
	17	0.93	109	62	
	18	0.93	97	55	STD.
25	19	0.93	110	62	DEV.: 3.92
	20	0.93	110	62	
	21	0.94	103	57	
	22	0.94	121	67	

- 26 -

TABLE 7

Acid Washed Slides &amp; PU/SiC Indented

These slides were fired at 400°C then washed in

1M HNO<sub>3</sub>. Then coated with PU containing 6.2% SiC whiskers

5 (US disp.)

	SAMPLE				SAMPLES	
	NUMBER	DEPTH	LOAD	MOR (MPA)		22
10	1	0.91	169	100	WEIBULL	
	2	0.91	130	77	MEAN:	7.63
	3	0.87	137	89		
	4	0.87	177	115	FIT OF	
	5	0.87	167	108	MEAN:	0.9498
	6	0.87	165	107		
	7	0.93	127	72		
15	8	0.93	127	72	WEIBULL	
	9	0.85	160	109	MEDIAN:	8.11
	10	0.85	110	75		
	11	0.89	161	100	FIT OF	
	12	0.89	148	92	MEDIAN:	0.9370
	13	0.92	147	85		
	14	0.92	147	85		
20	15	0.88	147	93	MEAN	
	16	0.88	137	87	M.O.R.:	91.10
	17	0.87	137	89		
	18	0.87	113	73	STD.	
	19	0.93	165	94	DEV.:	12.40
	20	0.93	169	96		
	21	0.91	172	102		
25	22	0.91	142	84		

As the fracture behaviour of the PU/SiC composite material was markedly different to the previous tests several fractures were recorded at a higher chart speed. The results of these experiments are shown in Figures 11 to 13.

5 The coating of glass with a composite of polyurethane and silicon carbide whiskers provides a remarkable increase in toughness. The fractured samples show a large increase in minor cracking and this provides stress dispersion (see Figures 14 and 15). When examined by  
10 scanning electron microscopy, the unfilled PU film showed a clean brittle fracture (Figure 17a), where as the filled PU coating (Figures 17b, c) showed evidence of crack branching or tearing, while the classical scheme of fibre pull-out was demonstrated. The result of this dispersion and fibre  
15 pull-out is a large increase in the energy required to fracture the glass. The Figures 11 to 13 clearly show a very large increase in area under the stress/displacement curve for the PU/SiC composite samples (Figure 13) compared to unreinforced PU (Figure 12) or uncoated glass (Figure 11).  
20 For Figure 13 it is important to note that the curved decay in stress starting at about 1.2 mm displacement is a result of the stress being removed; it is not the ultimate failure of the sample. The stress had to be removed since the sample had curved so much as to wedge in the biaxial testing rig and  
25 further results would have had little meaning.

- 28 -

Finally, it is to be understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention as outlined herein.

CLAIMS :

1. A glass coating composition including  
an effective amount of at least one inorganic or  
organic polymeric component; and

at least one reinforcing component incorporated  
therein;

the glass coating composition being such that when  
coated on a glass substrate it strengthens and toughens the  
article.

2. A glass coating composition according to claim 1  
wherein the at least inorganic or organic polymer component  
is a synthetic organic polymer selected from acrylate and  
methacrylate polymers or copolymers, acrylamide or  
methacrylamide polymers or copolymers, urethane polymers or  
copolymers, alkyd resins or mixtures thereof.

3. A glass coating composition according to claim 2  
wherein the synthetic organic polymers includes  
approximately 40% to 90% by weight, based on the total  
weight of the glass coating composition, of a polyurethane  
polymer.

4. A glass coating composition according to claim 1  
wherein the at least one reinforcing component is selected  
from components which have a platelet-type structure or a  
fibrous structure.

5. A glass coating composition according to claim 4  
wherein the reinforcing component is selected from silicon  
carbide or vermiculite having a platelet type structure and  
silicon carbide, silicon nitride, alumina and metals having  
a fibrous structure; or mixtures thereof.

6. A glass coating composition according to claim 5

- 30 -

wherein the at least one reinforcing component includes approximately 5 to 60% by weight, based on the total weight of the glass coating composition, of an exfoliated vermiculite.

5 7. A glass coating composition according to claim 1 further including an effective amount of at least one coupling agent.

8. A glass coating composition according to claim 7 wherein the at least one coupling agent includes  
10 approximately 0.1 to 1% by weight, based on the total weight of the glass coating composition, of an amino silane.

9. A glass coating composition according to claim 2 wherein, when the synthetic organic polymer is a water-soluble polymer, the glass coating composition further  
15 includes an effective amount of at least one cross-linking agent.

10. A glass coating composition according to claim 9 wherein the at least one cross-linking agent is present in amounts of from 0.1% to approximately 50% by weight, based  
20 on the total weight of the glass coating composition, of a heat or radiation curable cross-linking agent.

11. A glass coating composition according to claim 1 including

approximately 40 to 70% by weight of polyacrylamide;  
25 approximately 30 to 60% by weight of vermiculite; and  
approximately 0.1% to approximately 0.5% by weight of  
(N,N-diethyl-3-aminopropyl)trimethoxysilane.

12. A glass coating composition according to claim 1 including



approximately 80 to 95% by weight of a polyurethane polymer; and

approximately 5 to 15% by weight of silicon carbide.

13. A toughened article including

a glass article; and

a glass coating on at least on surface thereof formed from a glass coating composition including an effective amount

at least one inorganic or organic polymeric component;

and

at least one reinforcing component incorporated therein;

the glass coating being such that when coated on the glass article, it strengthens and toughens the article.

14. A toughened article according to claim 13 wherein the glass article is formed from a silica based glass.

15. A toughened article according to claim 13 wherein the glass coating composition includes

approximately 40 to 70% by weight of polyacrylamide;

approximately 30 to 60% by weight of vermiculite; and

approximately 0.1% to approximately 0.5% by weight of a coupling agent.

16. A toughened article according to claim 15 wherein the coupling agent is (n,n-diethyl-3-aminopropyl)-trimethoxy-silane.

17. A toughened article according to claim 13 wherein the glass coating composition includes

approximately 80 to 95% by weight of a polyurethane polymer; and

- 32 -

approximately 5 to 15% by weight of silicon carbide.

18. A toughened article according to claim 13 wherein the glass article is subjected to a purification step prior to application of the coating.

5 19. A process for preparing a toughened article including providing a glass article; and a glass coating composition including an effective amount of at least one inorganic or organic polymeric component; and  
10 at least one reinforcing component incorporated therein; the glass coating composition being such that when coated on a glass substrate it strengthens and toughens the article;  
15 contacting the surface of the glass article with the glass coating composition; and drying the coated glass article so formed.

20. A process according to claim 19 further including providing at least one coupling agent; and

20 mixing the coupling agent with the polymeric component and at least one reinforcing component for a time sufficient to allow the coupling component to hydrolyse and/or to interact with the reinforcing component prior to contact of the surface of the glass article.

25 21. A process for preparing a toughened article according to claim 19 wherein the at least one reinforcing agent is a vermiculite, said process further including the preliminary step of

subjecting the vermiculite to a conversion process to

produce an exfoliated vermiculite.

22. A process for preparing a toughened article according to claim 18 which process further includes the preliminary step of subjecting the glass article to a heat treatment elevated temperature for a time sufficient to clean the surface thereof.

23. A process for preparing a toughened article according to claim 21 wherein the heat treatment is conducted at temperatures approximately 350-450°C.

24. A process for preparing a toughened article according to claim 18 wherein the polymeric component is a water soluble organic polymer which process further includes

providing an effective amount of at least one cross-linking agent; and

subsequently curing the coated glass article.

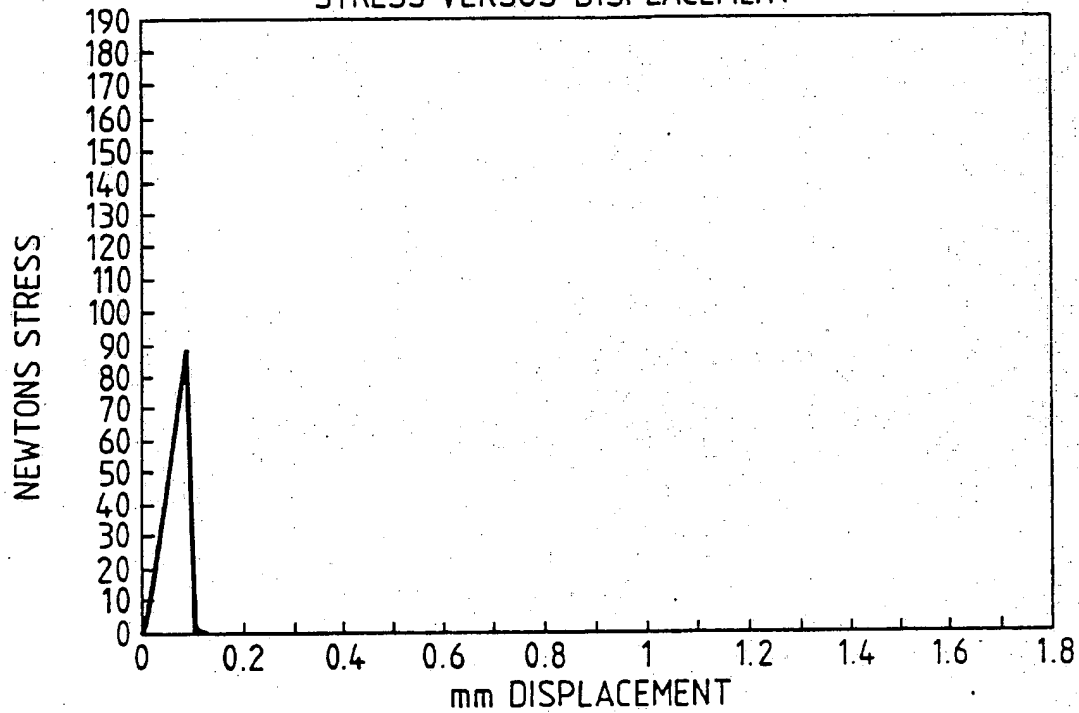
25. A process for preparing a toughened article according to claim 23 wherein the at least one cross-linking agent is a heat curable cross-linking agent and the curing step includes heating the coated glass article at elevated temperature for a period sufficient to provide substantially complete cure.

26. A process for preparing a toughened article substantially as hereinbefore described with reference to any one of the examples.

*Fig. 1.*

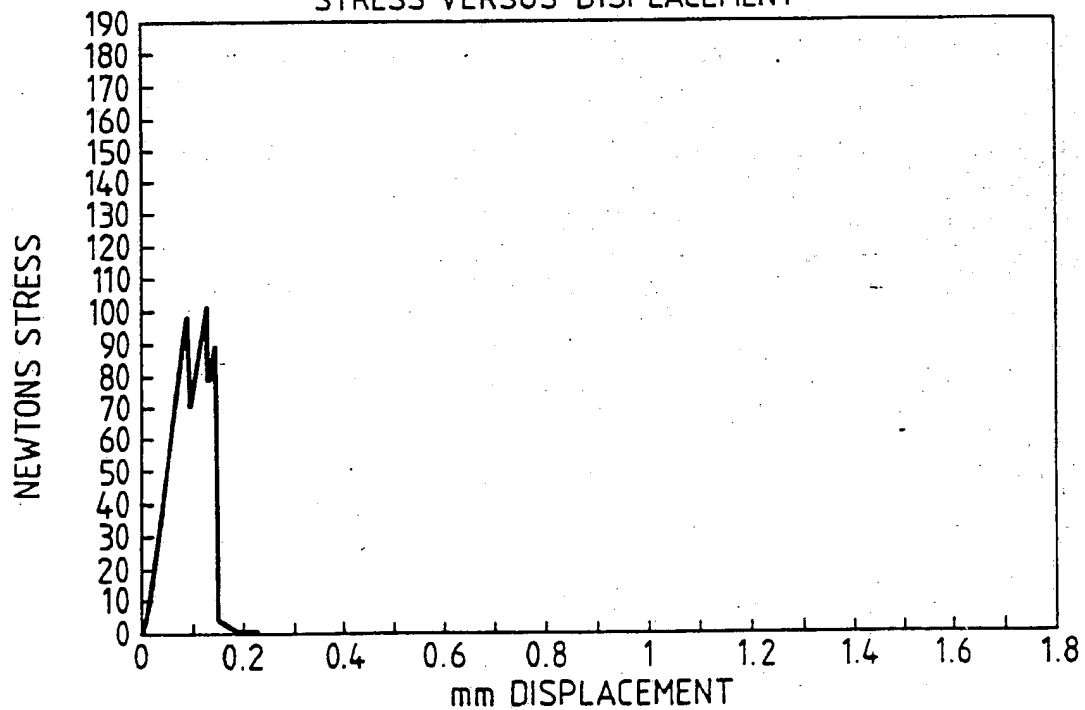
UNCOATED GLASS

STRESS VERSUS DISPLACEMENT

*Fig. 2.*

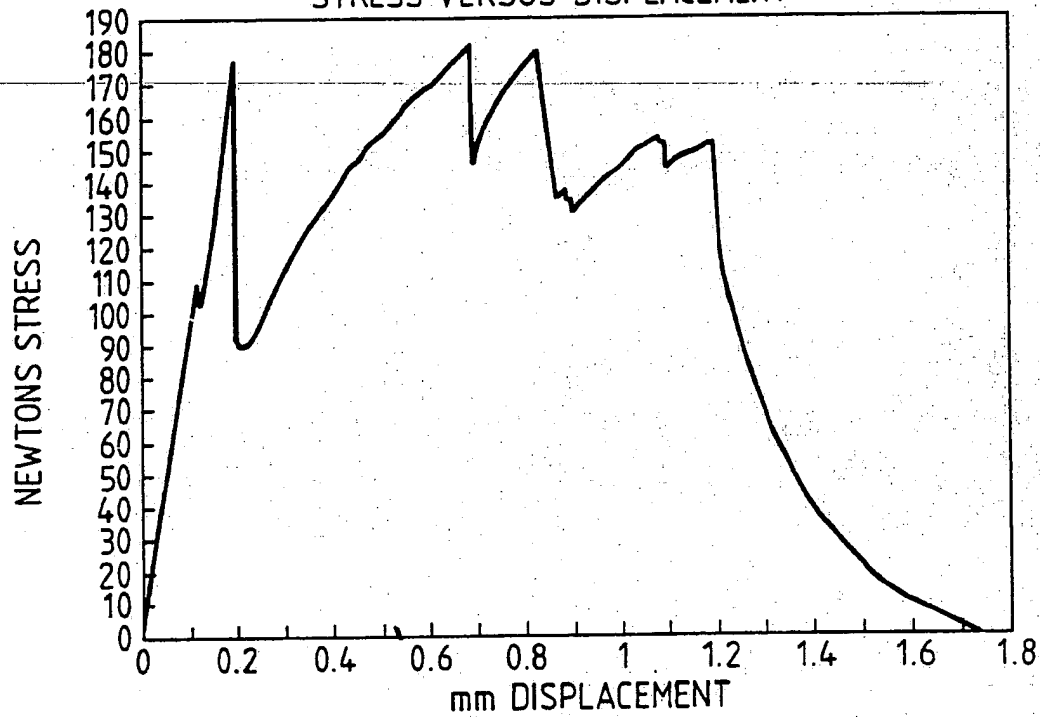
PU COATING - NO WHISKERS

STRESS VERSUS DISPLACEMENT

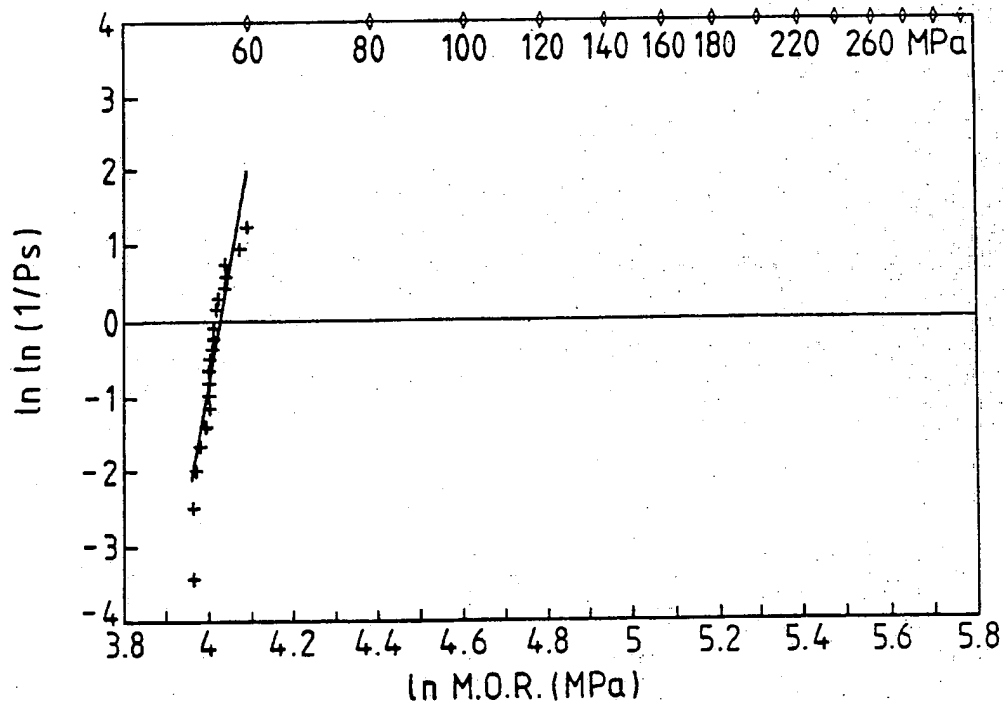


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*Fig.3.* PU/SiC COMPOSITE ON GLASS  
STRESS VERSUS DISPLACEMENT

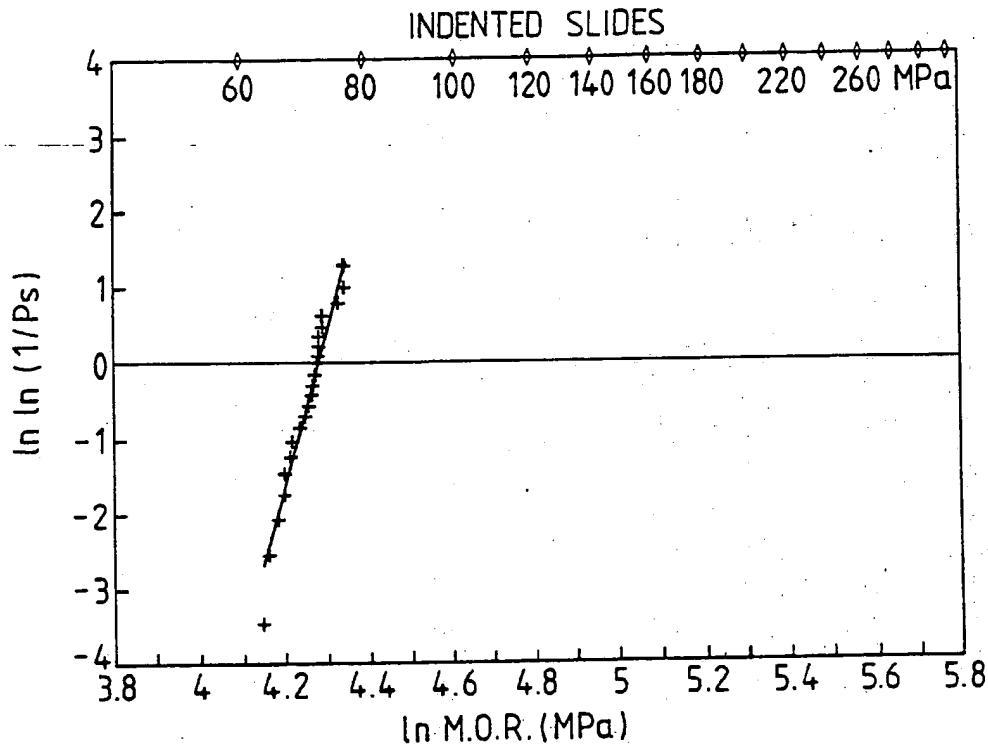


*Fig.4.* AS FIRED SLIDES, UNCOATED  
INDENTED / REFIRED

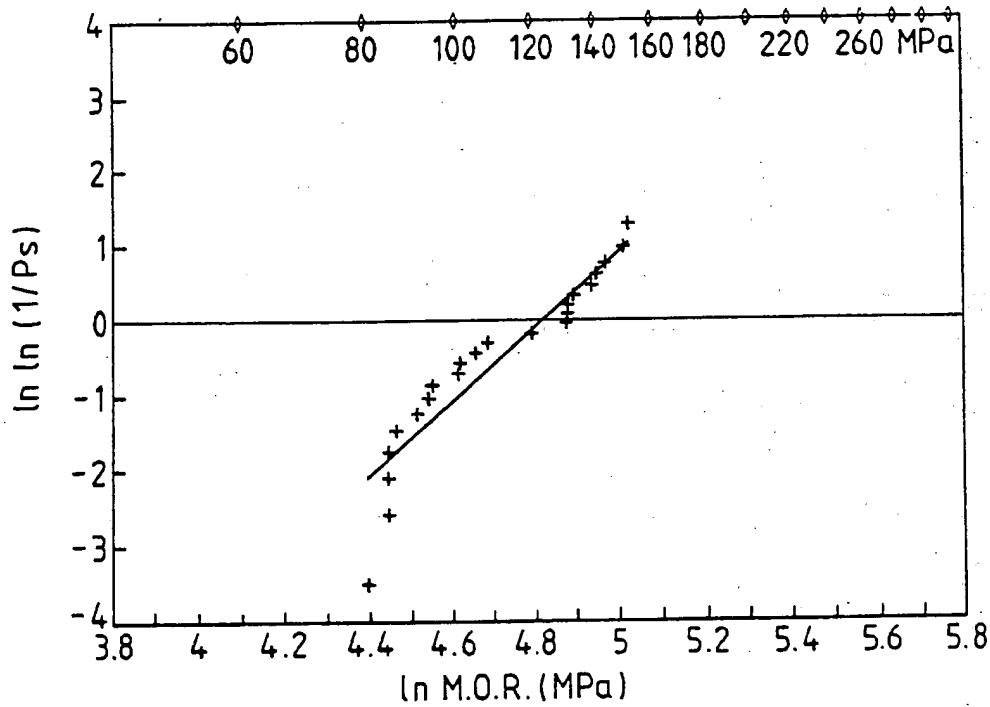


3/9

*Fig. 5.* FIRED SLIDES PU

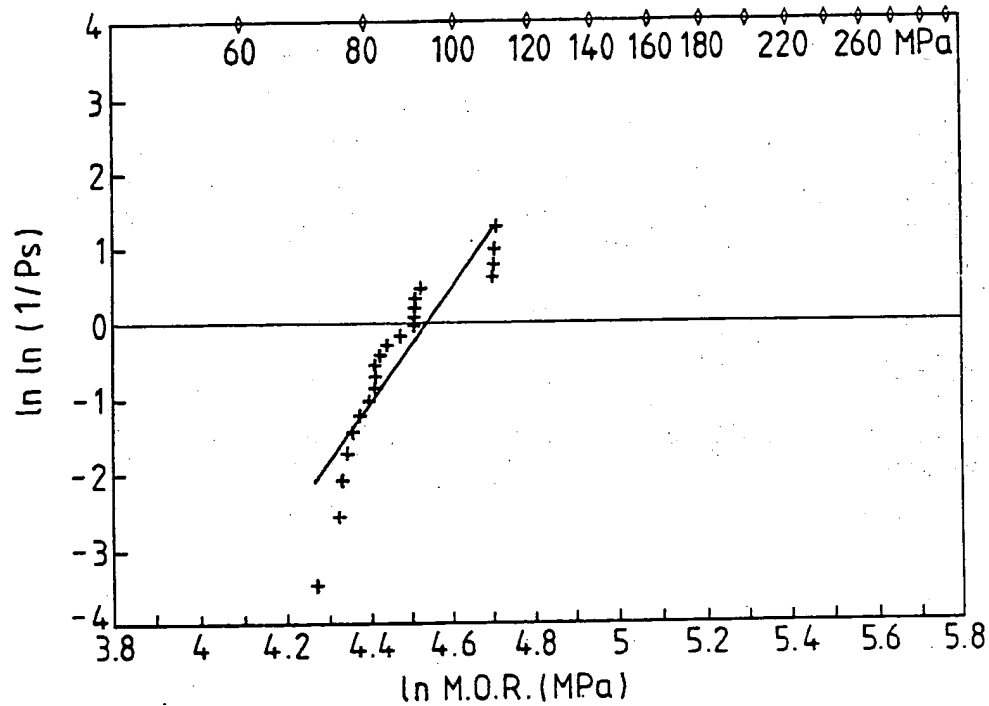


*Fig. 6.* FIRED SLIDES & 6.2% SiC/PU  
INDENTED SLIDES (US DISP.)

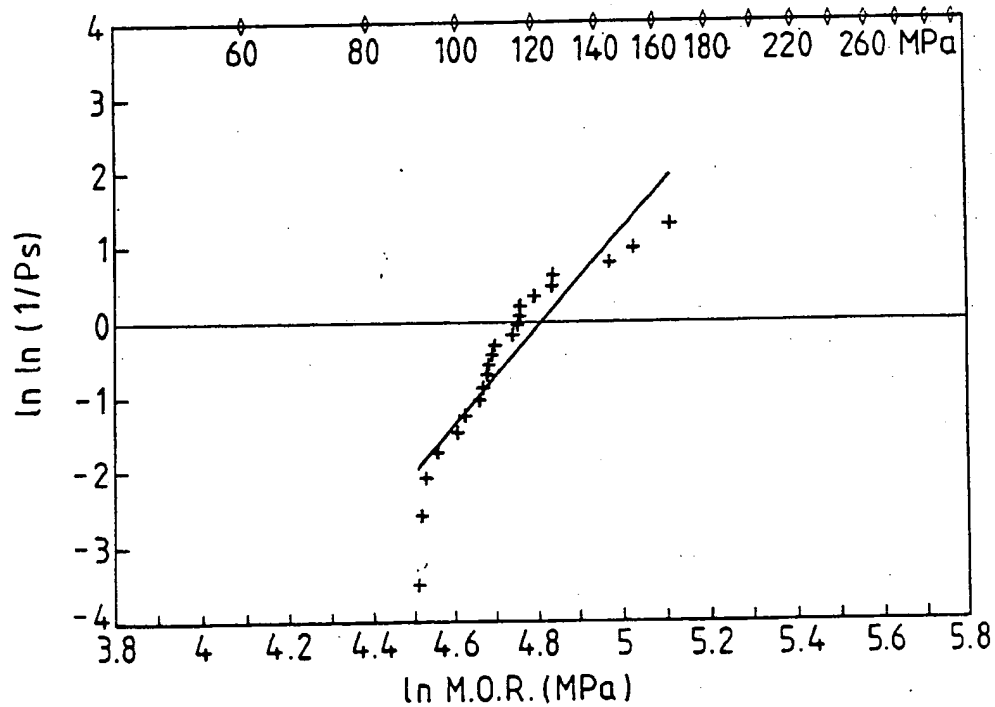


SUBSTITUTE SHEET

*Fig. 7.* FIRED SLIDES & 7.6% SiC/PU  
INDENTED SLIDES

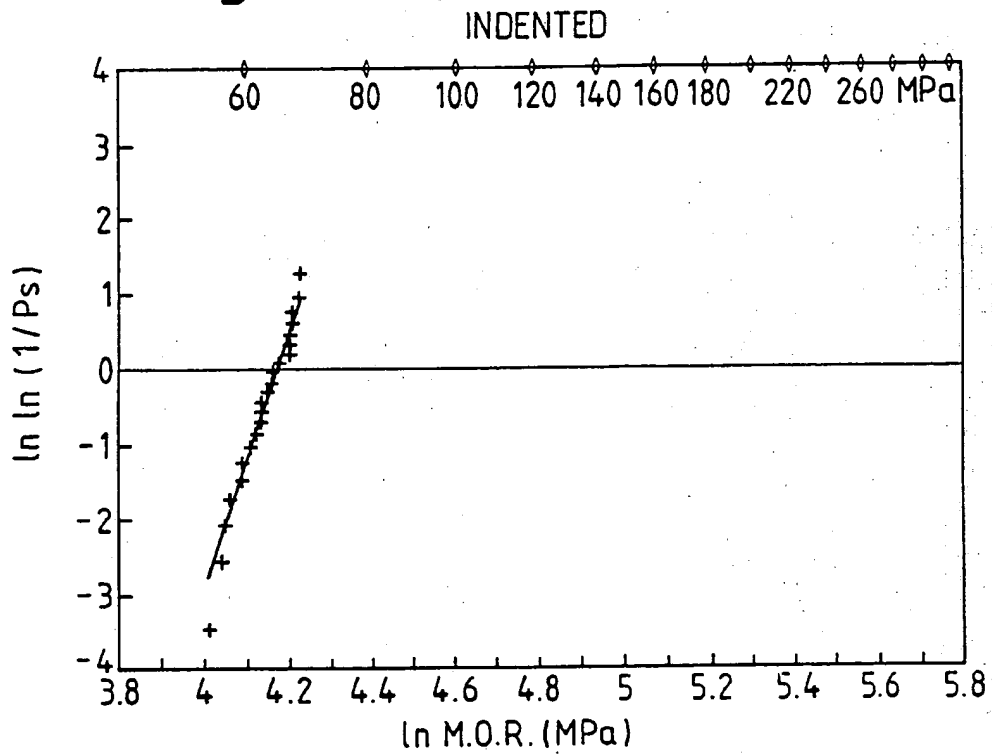


*Fig. 8.* FIRED SLIDES & 8.8% SiC/PU  
INDENTED SLIDES (US DISP.)

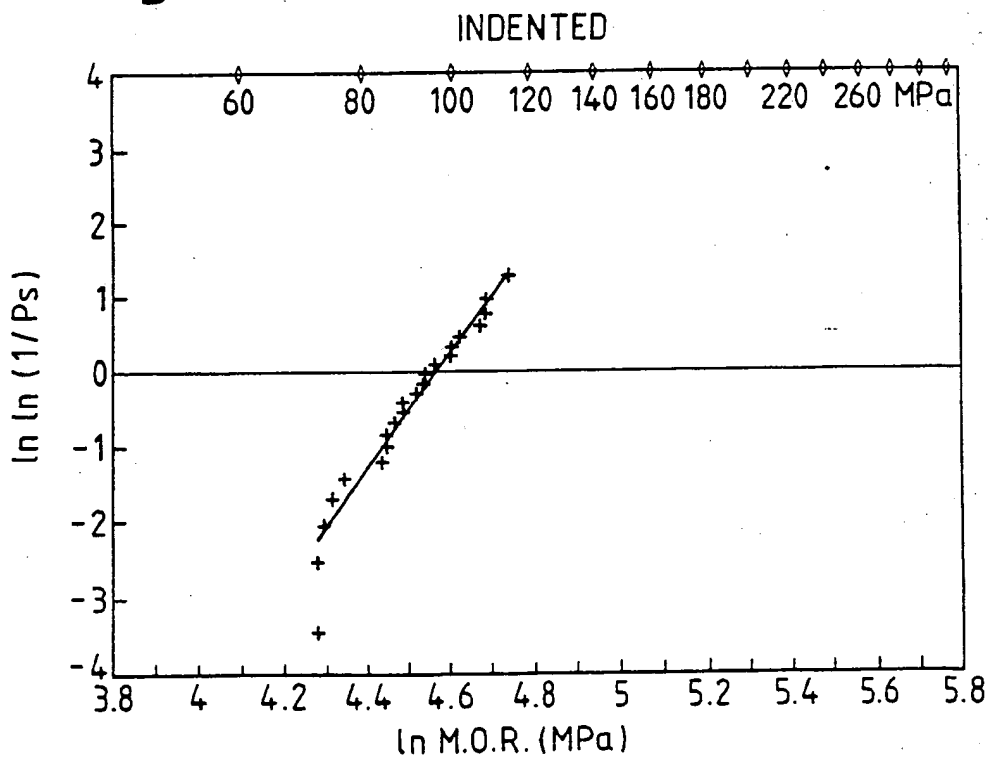


5/9

*Fig. 9.* ACID WASHED SLIDES

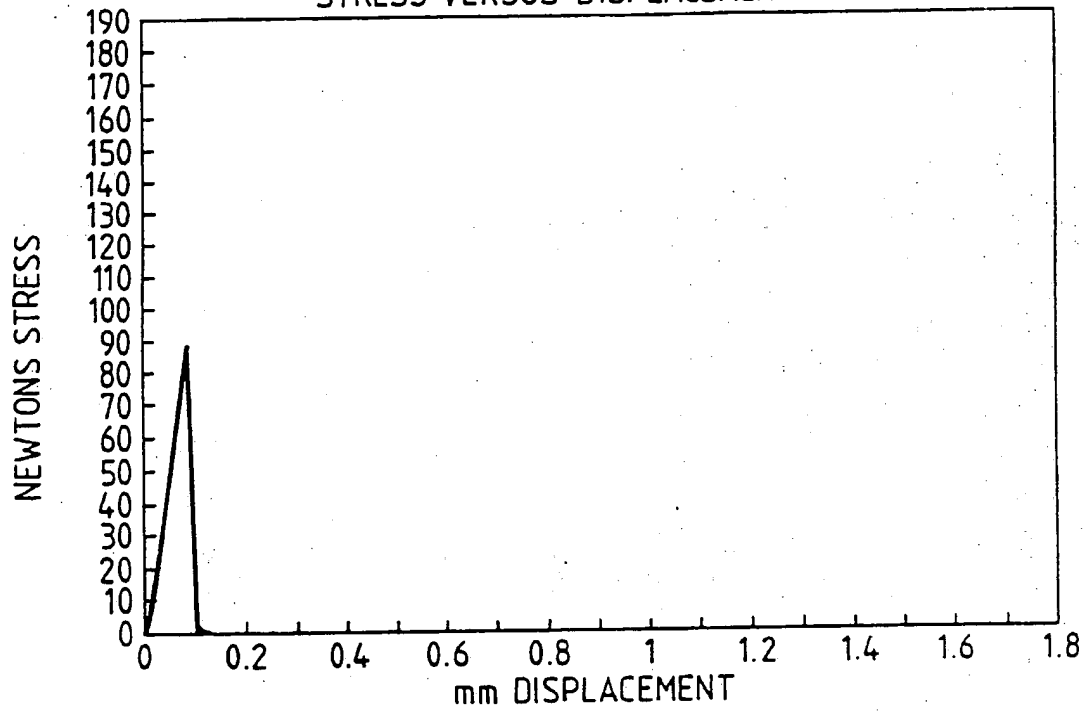
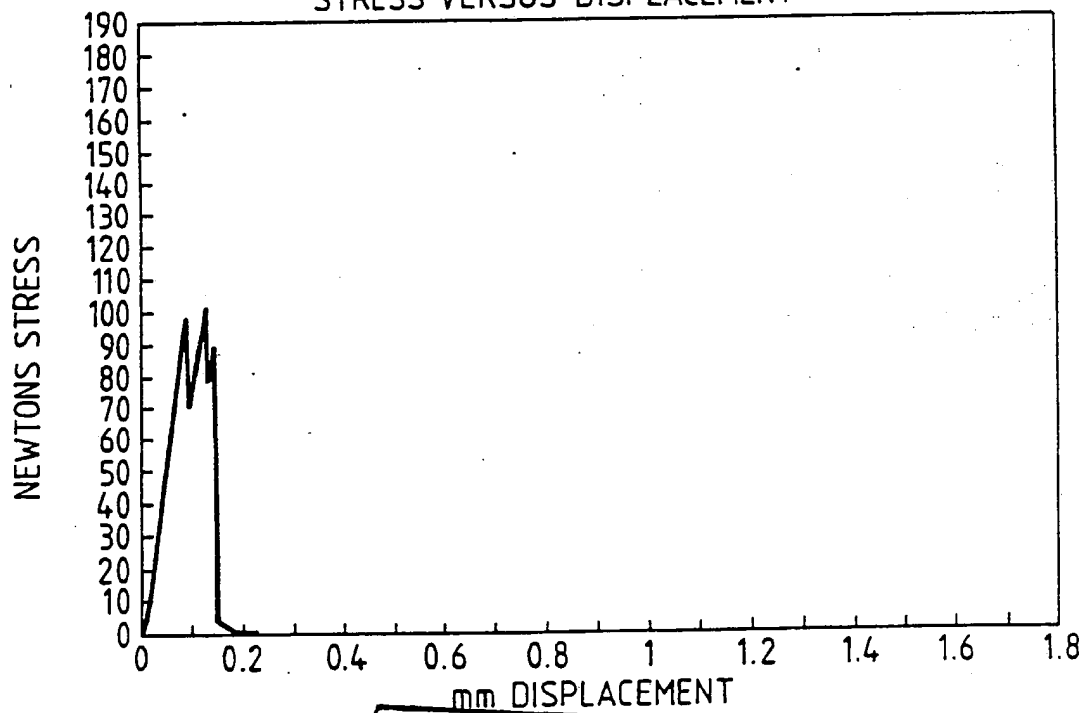


*Fig. 10.* ACID WASHED SLIDES & PU/SiC



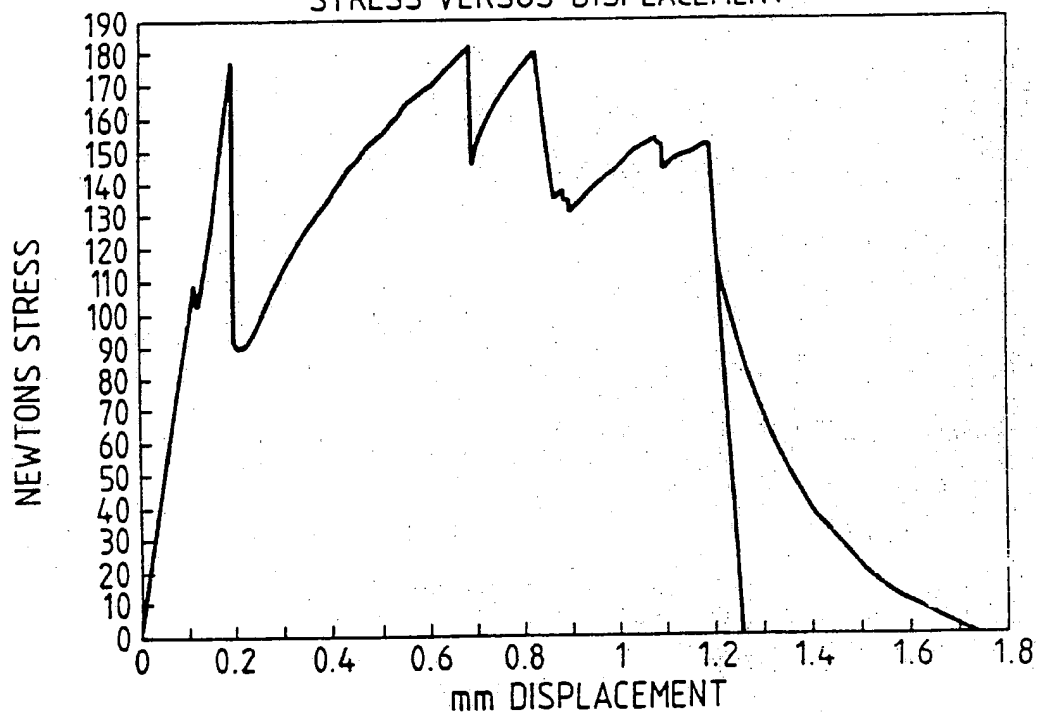
SUBSTITUTE SHEET



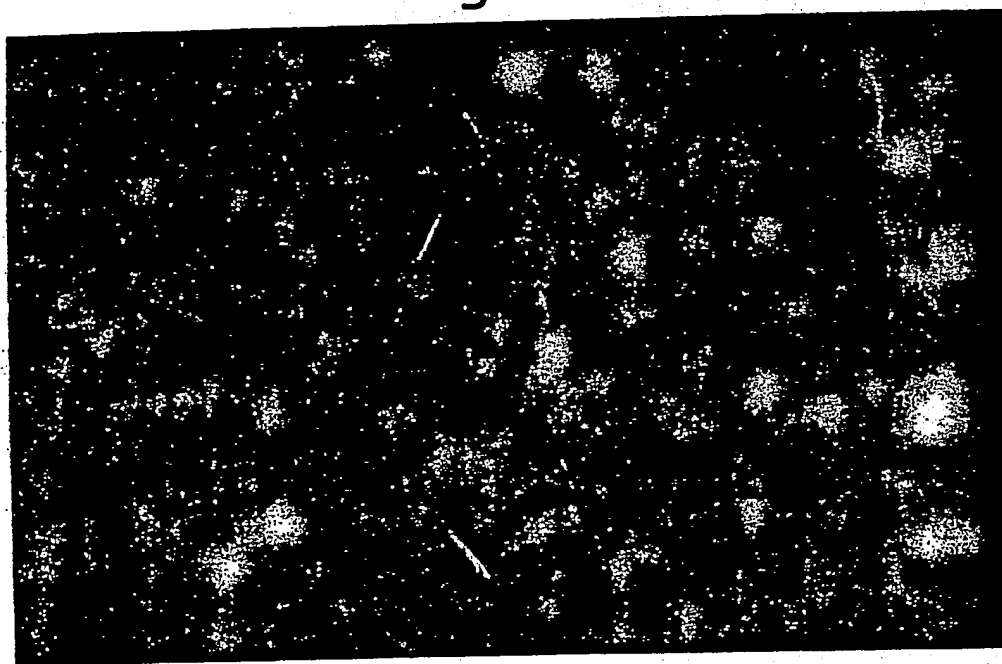
*Fig.11.*UNCOATED GLASS  
STRESS VERSUS DISPLACEMENT*Fig.12.*PU COATING - NO WHISKERS  
STRESS VERSUS DISPLACEMENT

SUBSTITUTE SHEET

*Fig.13.* PU/SiC COMPOSITE ON GLASS  
STRESS VERSUS DISPLACEMENT



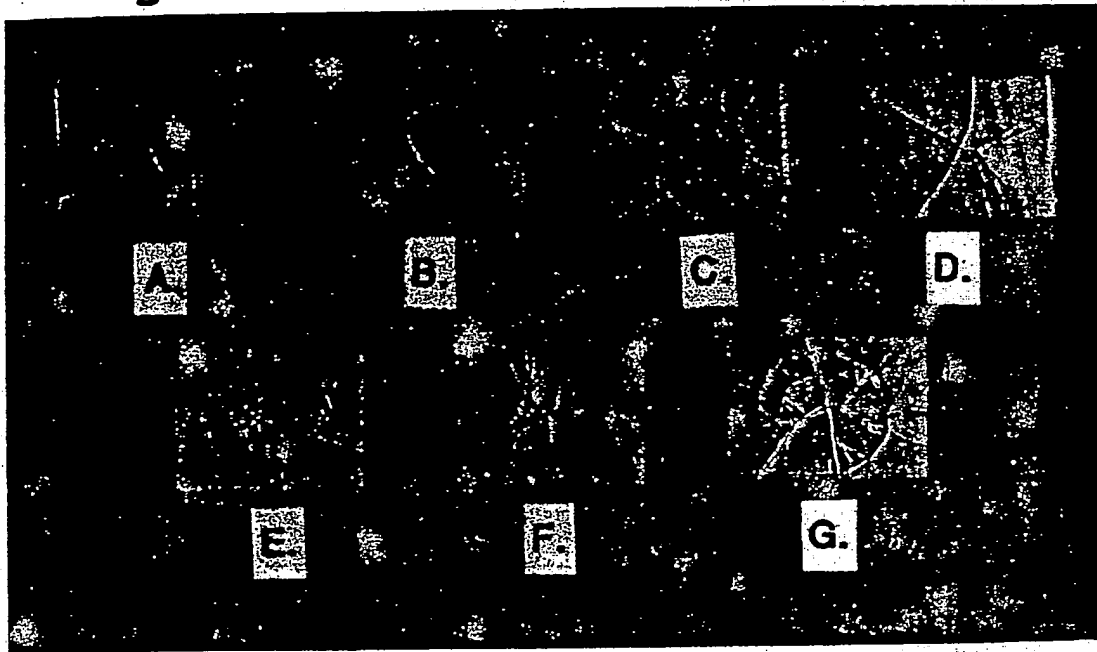
*Fig.14.*



THE DEVELOPMENT OF MINOR CRACKING DURING FRACTURE  
OF A GLASS SLIDE COATED WITH PU/SiC COMPOSITE.

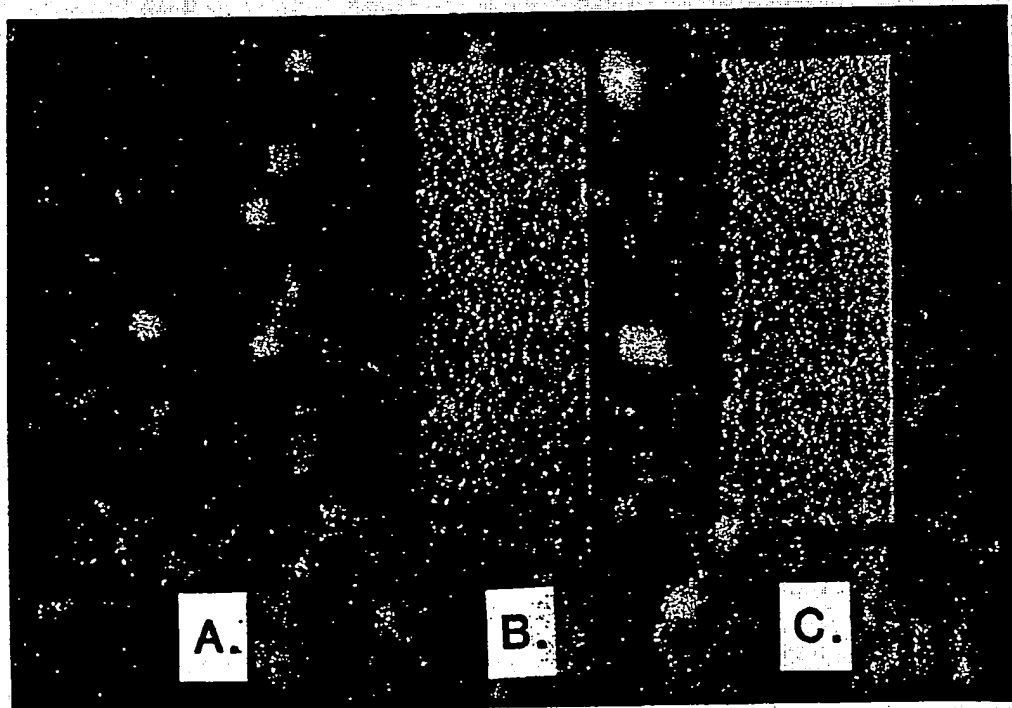
**SUBSTITUTE SHEET**

Fig. 15.



FRACTURED GLASS SLIDES :  
 A & B NORMAL UNCOATED SLIDES.  
 C - G SLIDES COATED WITH PU/SiC COMPOSITE.

Fig. 16.

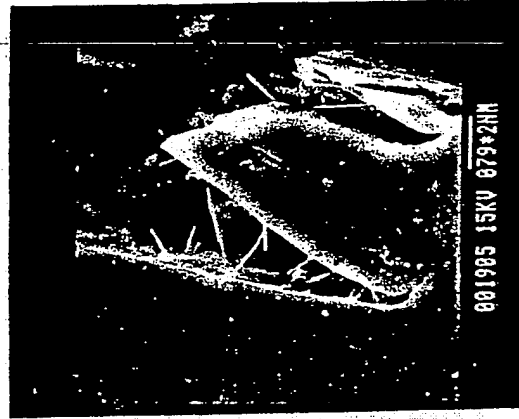


PU COATED SLIDES PRIOR TO FRACTURE :  
 A UNREINFORCED PU.  
 B PU/SiC DISPERSED BY STIRRING.  
 C PU/SiC DISPERSED BY ULTRA SONIC BATH.

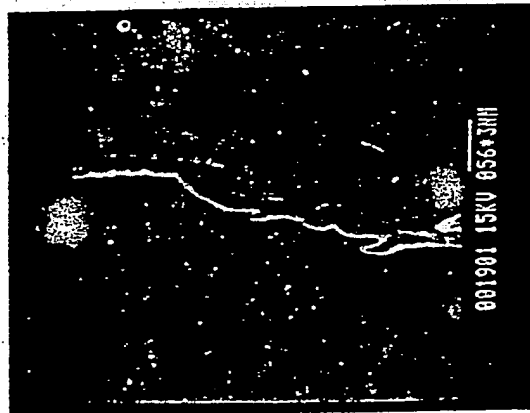
**SUBSTITUTE SHEET**

*Fig.17.*

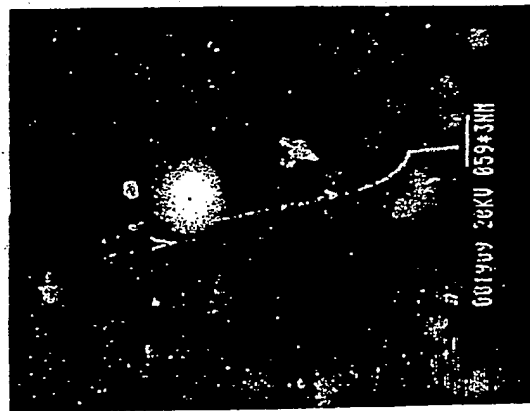
C.



B.



A.




SUBSTITUTE SHEET

SEM PHOTOGRAPHS OF CRACKS IN PU/SiC FILMS.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 89/00196

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) 6		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. <sup>4</sup> C03C 17/32, B32B 17/04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched 7		
Classification System	Classification Symbols	
IPC	C03C 17/32, B32B 17/04	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8		
AU : IPC as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> 9		
Category*	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
X,Y A A A A A A A A A	CA,A,1050223 (WIMMER) 13 March 1979 (13.03.79) US,A,4684694 (BREUER ET AL) 4 August 1987 (04.08.87) AU,B,58802/80 (525770) (SEKISUI KAGAKU KOGYO KK and TOKUYAMA SEKISUI KOGYO KK) 4 December 1980 (04.12.80) AU,B,41860/85 (583038) (SAINT-GOBAIN VITRAGE) 7 November 1985 (07.11.85) AU,A,24253/54 (168095) (MONSANTO) 11 March 1954 (11.03.54) US,A,3515579 (SHEPHERD ET AL) 2 June 1970 (02.06.79) US,A,3805985 (HAGIWARA ET AL) 23 April 1974 (23.04.74) US,A,4143181 (CAHN ET AL) 6 March 1979 (06.03.79) US,A,4280944 (SAITO ET AL) 28 July 1981 (28.07.81) US,A,4510282 (GOLL) 9 April 1985 (09.04.85)	(1,2,13,14,19)
* Special categories of cited documents: 10		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family	
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 14 July 1989 (14.07.89)	Date of Mailing of this International Search Report 21 July 1989 (21.07.89)	
International Searching Authority Australian Patent Office	Signature of Authorized Officer  P. MALANOS ASE	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON  
INTERNATIONAL APPLICATION NO. PCT/AU 89/00196

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members		
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AU	41860/85	BR 8502047 ES 542751 FR 2563754 NO 851499 US 4783344	DK 1884/85 ES 8700975 IN 164462 NZ 211646 YU 692/85	EP 162756 FI 851705 JP 60241972 PT 80371 ZA 8502743
US	3515579	BE 734873 GB 1260948 IT 1044802 FR 2011364	CH 530876 GB 1262250 NL 7400531 US 3488215	DE 1928409 IL 32426 BR 6909889
US	3805985	DE 2149219 JP 48052737	FR 2110164	GB 1356333
US	4143181	AR 215266 BE 856445 CH 623017 ES 461276 GB 1570742 LU 77705 NO 772729 ZA 7704144	AT 5205/77 BR 7705061 DE 2732062 FI 772345 IT 1083449 MX 147518 NZ 184805 FR 2395962	AU 27590/77 CA 1097541 DK 3453/77 FR 2360523 JP 53041319 NL 7708358 SE 7708673
US	4280944	AU 57982/80 JP 56000819	EP 19368 NZ 193625	IL 59508
US	4510282	DE 3102169	EP 57813	GB 2095265